terized by their low internal energy so that it can be easily detected at low voltage, where fragmentation is negligible.

[0094] Five different acids from formic acid to pentanoic acid have been detected in negative mode and the spectra are shown in FIGS. **15**A-E. Each spectrum is characterized by the presence of a proton bound dimer along with the molecular ion peak. Another finding was the detection of mixed dimers at low voltage. Here various acid combinations were made and were analyzed at low voltage of 1V. The results are demonstrated in FIGS. **16**A-D. Here, a variety of mixed dimers were seen along with the expected individual acid dimers.

[0095] The variation of intensity of these acid dimers with voltage (D/M ratio vs voltage) has been tested and the results show a gradual decrease in the intensity of acid dimers as we go to very high voltages. FIGS. **17**A-B represent the results, where D/M ratio has been plotted as a function of voltage for five different acids in two different solvents (water and methanol). Similar study was carried out on a single acid in different solvents also. Here propionic acid was taken in different solvents and the D/M ratio was noted for a range of voltage from 1 V to 3 kV. Result is shown in FIG. **18**.

[0096] Another set of study was carried out at low voltage (1V) on different anionic species where the aim was to detect various hydrates of anions. The results are shown in FIGS. **19**A-D. The results show the presence of various hydrates of different anionic species from chloride to acetate.

Example 4

Spray Formation

[0097] This Example investigates the mechanism of low voltage spray. In order to establish the mechanism of this spray two pathways were taken, e.g., study of changing signal to noise ratio upon increasing low voltage to moderately high voltage (500 V), secondly, by capturing video during the spray. Besides these work, some effort was given on computational study to support the work. It is proposed that several mechanisms may be responsible (operating independently or collectively) to give rise to signal at very low voltage. Detection of microorganisms at low voltage is shown as an application of this method.

[0098] In order to understand the mechanism, a few experiments were performed. Analytes, such as, triphenylphosphine (PPh_3), tricyclohexylphosphine, dibutylamine, tributylamine were utilized in the experiments. One such example is given below.

[0099] In an experiment, 5 μL 50 ppm PPh_3 was sprayed into the mass spectrometer. The spray voltages were varied from 2 V to 500 V. This investigation was stopped at 500 V for two reasons. Firstly, to avoid any discharge arising from the CNT coated paper tip. Secondly, above 500 V spray voltage, the signal intensity increased rapidly and was reaching values comparable to normal paper spray.

[0100] The tip was held at a separation ~0.5 mm from mass spec inlet. Spectra were collected and analyzed and the signal to noise ratio (S/N) and signal intensity with respect to increasing spray voltage was plotted (FIGS. **20** and **21**). The distribution is divided in four regions. Region 1, 2 V spray where the analysis was commenced, no signal. Upon increasing the spray voltage to 3, 4 or 5 V, the S/N ratio shows rapid increase (region 2). Region 3, 8-500 V, the S/N ratio is at steady state. Beyond 500 V (region 4) the signal/noise rises rapidly but is not shown as it tends towards normal paper spray values. After 500 V, the signal increases to two or three orders of magnitude compared to low voltage spray so normal paper spray (PS) comes into play at this voltage.

[0101] The appearance of analyte signal is controlled by two factors, field emission and field-induced transport of the ionized molecule (in a thin film of solution) to the high field (emitter) areas of the substrate. A hypothesis is that at very low voltage (Region 1) the small number of molecules already in place at high field spots are ionized by field emission, presumably in microdroplets. This requires a limited voltage in combination with the small physical dimensions (order of 1 nm). So 5 V at 1 nm gives a field strength of 5×10^9 V/m which is just in the range of field emission (Beckey, Field Ionization Mass Spectrometry, Pergamon, London, 1971). Region 2 (5-300 V) is approximately a steady state region in terms of S/N ratio in terms of signal there are two sub-regions, 5-100 V where the signal falls and 100-300 V where it rises slightly. These data mean that either the field emission is slow, and rate limiting, or the field induced transport is slow. One expects an increase in field emission with voltage (if for no other reason than the fact that the area in which the field strength exceeds that needed for ion formation is increasing). However, if transport is not effective, this signal can fall with increasing voltage because of prior removal of material from the higher field areas. It is proposed that the transport of material related to PPh_3 only becomes effective around 100 V. The break at 300 V might be due to different mechanisms of transport, such as solution phase vs. thin film or conversion to an ion here and very effective transport.

Example 5

Microorganism Analysis using Probes of the Invention

[0102] For microorganisms, the bacteria isolates, supplied by bioMérieux, Inc. (Hazelwood, MO) were cultured from frozen samples stored at −80° C. on TSAB in cryotubes. All experiments were performed under Institutional Review Board guidelines IBC protocol #07-004-10 "Novel tissue, Biological fluid and Bacteria Evaluation by Mass Spectrometry" as amended. Five types of microorganisms were used in the present study, which are *Escherichia coli* (Gram-negative bacteria), *Citrobacter farmeri* (Gram-negative bacteria), *Staphylococcus aureus* (Gram-positive bacteria), *Bacillus subtilis* (Gram-positive bacteria), *Saccharomyces cerevisiae* (yeast). These common microorganisms are chosen due to their widespread presence throughout the biosphere.

[0103] Microorganism samples (*Bacillus subtilis* in this case) were analyzed using CNT spray and paper spray. *Bacillus subtilis* can be detected using low voltage spray using CNT coated paper and their mass spectra are comparable (FIGS. **22**A-B) to traditional paper spray. However, at 3 V, the mass spectra intensity is usually three orders of magnitude less intense than normal paper spray signal (FIG. **22**B). Reproducibility was tested by analyzing *Citrobacter fameri* seven times. In each mass spectrum a similar relative abundances of lipids was obtained.

1-20. (canceled)

21. A method for analyzing a biological molecule, the method comprising: